

recorded method¹¹, was dissolved in water (45 ml), and a solution of thiocarbonyl chloride (6.1 g) in chloroform (50 ml) was added. To the vigorously shaken mixture 1.4 N NaOH (76 ml) was slowly added. After 0.5 hour, the chloroform layer was separated, dried and evaporated. Distillation *in vacuo* of the residue afforded 5.1 g (60 %) of the isothiocyanate, b.p. 136° at 12 mm, with a characteristic smell of radish. Ref.³ lists b. p. 130—140° at 9 mm.

The mustard oil was dissolved in ethanol, previously saturated with ammonia at 0°, and left at room temperature for 3 days. The solvent was removed and the residue recrystallized twice from water and once from chloroform and petroleum ether before analysis. M. p. 53° (Fisher-John's block). Ref.³ reports m. p. 55—56°. (Found: N 15.80; S 36.07. Calc. for C₆H₁₄N₂S₂: N 15.72; S 35.96).

N-(4-Methylthiobutyl)-*N'*-benzylthiourea (III). A solution of (I) (615 mg) and benzylamine (735 mg) in ethanol (3 ml) was kept at 40° for 18 hours. The solvent was then removed and the residue taken up in ether. The solution was shaken with small portions of 0.5 N HCl and water in order to remove the excess amine. During these operations the separation of the crystalline thiourea started (900 mg). Before analysis, the sample was recrystallized twice from 70 % ethanol and once from ethyl acetate and petroleum ether, m. p. 77—78° (water bath). (Found: C 58.25; H 7.55; N 10.45. Calc. for C₁₃H₂₀N₂S₂: C 58.15; H 7.51; N 10.44. Calc. for C₁₁H₂₅N₂S₂: C 58.28; H 6.44; N 10.81).

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1. Kjær, A., Conti, J. and Larsen, I. *Acta Chem. Scand.* 7 (1953) 1276.
2. Schmid, H. and Karrer, P. *Helv. Chim. Acta* 31 (1948) 1497.
3. Schultz, O.-E. and Gmelin, R. *Z. Naturforsch.* 8b (1953) 151.
4. Hals, S. and Gram, J. F. *Landwirtsch. Vers. Sta.* 70 (1909) 307.
5. Mohammad, A. and Ahmad, S. *Indian J. Agr. Sci.* 15 (1945) 181; *Chem. Abstracts* 42 (1948) 3139.

6. Sudborough, J. J., Watson, H. E. and Ayyar, P. R. *J. Indian Inst. Sci.* 9A (1926) 25; *Chem. Zentr.* 1926 II 2729.
7. Schneider, W. and Kaufmann, H. *Ann.* 392 (1912) 1.
8. Schmid, H. and Karrer, P. *Helv. Chim. Acta* 31 (1948) 1017.
9. Lavine, T. F. *Federation Proc.* 4 (1945) 96.
10. Kjær, A. and Rubinstein, K. *Acta Chem. Scand.* 7 (1953) 528.
11. Kjær, A. and Conti, J. *Acta Chem. Scand.* 8 (1954) 295.
12. Sjöquist, I. *Acta Chem. Scand.* 7 (1953) 447.

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The Calculation of Sedimentation Velocity from Experiments with Concentrated Mixtures

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A sedimenting boundary in the ultracentrifuge is by no means mathematically simple even in the case of a dilute solution of an ideal solute, as is seen from Faxén's¹ solution of the concentration function in a centrifuge cell. Additional complications, to which considerable attention has been paid, arise from thermodynamic and frictional effects, and from polydispersity. Thus the situation may be very complicated and is still more accentuated if the solution is concentrated *in a more hydrodynamic sense*², in which case the general form of the differential equation describing the course of the concentration change in the cell is intricate, even apart from effects of the non-constancy of the thermodynamical and frictional coefficients.

In such a situation it may sometimes seem more natural to use the concentration decrease in the middle of the sector-shaped cell than to use an analytical property of the boundary. This well-known possibility is evident from the considerations of Rinde^{3,4}, of Trautman and Schumaker⁵ and others.

In a part of the cell, not reached by the diffusion gradient regions at the top and bottom, the determination of the actual sedimentation coefficients of a two-com-

ponent system is quite simple even in the cases of the most complicated boundaries indicated above.

Disregarding the diffusion term, the two-component case is described by (cf. Ref.², eq. (11); V is the partial specific volume)

$$\frac{\partial m_2}{\partial t} = -\frac{1}{x} \frac{\partial}{\partial x} \left(\frac{m_1^2 m_2^2 (V_1 - V_2) V_1 \omega^2 x^2}{\varphi_{12}} \right) \quad (1)$$

Rinde showed for this non-diffusion case that the concentration decrease during the process is uniform over the cell and is thus the same at different levels. This statement is a consequence of the condition of continuity and does not assume a dilute system. However, it assumes that we start from a constant composition in the cell. Such being the case, we have the advantage that the concentrations m_1 , m_2 g/cm³ and the friction per cm³ φ_{12} are independent of x , which reduces equation (1) to

$$\frac{\partial m_2}{\partial t} = -2m_1^2 m_2^2 (V_1 - V_2) V_1 \omega^2 / \varphi_{12} \quad (2)$$

The sedimentation coefficient of component 2 is³

$$s_2 = m_1^2 m_2^2 (V_1 - V_2) V_1 / \varphi_{12} \quad (3)$$

which, by substituting equation (2), can be consequently determined from

$$s_2 = -\frac{1}{2m_1 \omega^2} \frac{\partial m_2}{\partial t} \quad (4)$$

by an experimental determination of $\partial m_2 / \partial t$ somewhere in the middle of the cell.

Equation (4) is the same here as in the theory of the sedimentation of a dilute substance. As already mentioned, the equation assumes a uniform concentration over the cell. We will stick to this restriction but will drop now the restriction to two components. For the i th component, the continuity equation for the "cylindrical" flow in the cell of sector shape is

$$\frac{\partial m_i}{\partial t} = -\frac{1}{x} \frac{\partial}{\partial x} (s_i m_i \omega^2 x^2) = -2s_i m_i \omega^2 \quad (5)$$

where $s_i \omega^2 x$ is, by definition, the sedimentation velocity in cm/sec. For any partial quantity, in this case the partial volume \bar{V}_i , $\Sigma \bar{V}_i dm_i = 0$. Combined with equation (5) this gives an equation previously proved for two components

$$\Sigma s_i m_i \bar{V}_i = 0 \quad (6)$$

The deduction shows that this special relation is not restricted to constant partial volumes, as distinct from the special

relations which connect sedimentation coefficients with frictions, which were reported elsewhere³.

It is often more practical to measure the change of refractive index n . Applying the approximation introduced previously³ in writing the refractive index n of the mixture

$$n = n_1^\circ m_1 V_1^\circ + n_2^\circ m_2 V_2^\circ \quad (7)$$

(where the index $^\circ$ refers to the pure component) and, in addition, assuming $V_1 = V_1^\circ$ and $V_2 = V_2^\circ$ as in the case of an ideal mixture, s_2 may be calculated according to

$$s_2 = \frac{\partial n / \partial t}{2(n_1^\circ - n) \omega^2} \quad (8)$$

n_1° is the refractive index of the medium, n that of the solution as measured in the cell during the experiment. The general expression $m_1 V_1 + m_2 V_2 = 1$ has been used in the deduction. As symmetry has been preserved, a corresponding approximate expression is valid also for s_1 . Equations other than (7) are not considered here.

Owing to its simplicity, expression (8) seems to be worth notice even if more exact expressions may prove necessary in many instances. Several-component cases must be specially considered. When using this procedure of measuring s for low-molecular mixtures, much will depend on the control of temperature, the sensitivity being excellent in itself if interference methods of observation are employed.

Conclusions. Owing to the complicated nature of a sedimentation boundary, it may sometimes be of value to use the general concentration change in the middle of the cell, the theory of which remains simple also in experiments with concentration effects. Some remarks are made on this procedure, which possesses a practical applicability also for the non-dilute system, the theory of which was treated in an earlier communication without mentioning any mode of practical calculation.

1. Faxén, O. H. *Arkiv Mat. Astron. Fysik* **21 B** (1929) No. 1.
2. Lamm, O. *Acta Chem. Scand.* **7** (1953) 173.
3. Rinde, H. *Dissertation*, Uppsala 1928.
4. Svedberg, T. and Pedersen, K. O. *The Ultracentrifuge*, Oxford 1940 (Leipzig 1940).
5. Trautman, R. and Schumaker, V. J. *J. Chem. Phys.* **22** (1954) 551.

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